POROSITY OF APCS COALS: THE ACCESSIBLE NATURE OF COAL IN THE PRESENCE OF SWELLING SOLVENTS

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ABSTRACT

A review will be given of the current status of spectroscopic techniques used to study the porous structure of coal with emphasis placed on the recent application of the EPR spin probe method to the study of Argonne Premium Coal Samples (APCS). The spin probe method has provided valuable insight into micropore size and shape characteristics during the swelling process. This technique also proved to be sensitive to changes in the coal structure brought about by variations in swelling solvent polarity, swelling temperature and other modifications of experimental conditions during the swelling process. Successive experiments showed that monitoring the accessibility of spin probes to the pore structure of coal could be used to follow the physical and chemical changes in coal during the weathering process, and to distinguish between the effects of dehydration and oxidation for periods as short as 30 seconds. Some of the results of long term weathering for periods upto six months of exposure to air will be discussed.

INTRODUCTION

The porous structure of coal has been of concern for many decades. Catalysis in the conversion of coal is generally related to the surface area available to the catalyst. Since most of the surface area of coal lies in the micropore structure of the coal, the determination of this structure and its effect on catalyst accessibility are important in coal conversion.[1,2] The most popular and versatile method for determination of the porous structure of coal is the gas adsorption method. Although this method provides more information than Hg porosimetry or other physical methods, it does have some severe limitations.[3] Several studies have given contradictory data and it has been shown that micropore volumes can vary by more than an order of magnitude when different gases are used.[4] This leads naturally to spectroscopic or imaging methods.

SANS, SAXS and light scattering: In the mid 1980's, methods using small angle neutron diffraction and small angle x-ray diffraction were used with success to characterize the shape and size of the micropores in Illinois # 6 coal.[6-11] It was determined from these studies that the micropores in low-ranked coal had elongated cylindrical shapes which had diameters of about 5.2A. More recently, SAXS has been used to study the pore structure during fluid extraction.[5] It was shown that micropore dilation was an irreversible process, whereas swelling of the macropore system was a reversible process.[5] In 1981, Kalliat et. al. used small angle x-ray scattering to show that there were three classes of pore systems in coal.[6] These results were somewhat consistent with adsorption data interpretation at that time. Small angle x-ray scattering was used later on by Setek et. al. in 1983 to determine the micropore structure of brown coal.[7] SAXS has also been used by Nemmers et. al. in 1990 to study the porous structure of coal during fluid extraction.[5] During various stages of fluid extraction of coal with THF, small angle x-ray scattering experiments showed that the extensive micropore structure formed during fluid exposure played a key role in the interaction between the fluid and the coal matrix needed for substantial extraction yields.[5] It was determined by Tricker et. al. in 1983 that small angle neutron scattering could be used to effectively determine pore size distributions in various ranked coals.[9] They felt that since the data obtained were substantiated by gas adsorption techniques, SANS could be used to probe coal porosity under circumstances where gas adsorption techniques were either severely limited or not possible.[9] Likewise, in 1983, Kaiser and Gethner also used small angle neutron scattering to study pore distributions and pore accessibility in coal.[10] It was determined that D_2O was not able to penetrate uniformly through dried coals.[10] Later, in 1986, Gethner used SANS to determine the void structure of Illinois #6 coal.[3] He determined that the microvoid volumes were elongated and possessed a well defined circular crossection of about 25A.[3] Also by comparison of aqueous and non-aqueous solutions, it was determined that the surface of the microvoid volume was primarily aliaphatic.[3] In 1987, Gethner used SANS and a combination of light scattering and absorption measurements to show that coal is a continuous distribution of voids rather than a well defined, discrete pore distribution, and to separate chemical changes from physical changes in coal during treatment and reactions.[11]

<u>SEM and imaging techniques</u>: Another technique used recently involves SEM analysis during liquid metal infiltration to provide direct imaging of the micropore system.[12] In 1991, Cody and Davis were able to directly image the pore space available to liquid metal (Wood's alloy) in a variety of coal ranks using SEM analysis.[12] They determined that the pores in the lowest rank coal were roughly cylindrical in shape, but that they constituted a rough particle surface and not an interconnected cylindrical pore network.[12] Pore space available to liquid metals in bituminous and higher ranked coals appeared to be made up entirely of microcracks.[12] Around this time, magnetic resonance imaging was also used to study pore structures during swelling.[13] It was shown that coal swells anisotropically; that is, solvents enter the bedding planes and thus the solvent is not distributed uniformly in the coal structure.[13]

NMR spin lattice relaxation and proton NMR

Glaves et. al. showed in 1988, that pore size distributions could be derived by deconvoluting measurements of the NMR relaxation spectra and applying a model to the pore fluid behavior.[14]

<u>Xe129 NMR</u>: Recently, Xe129 NMR studies have been used to determine average micropore volumes and diameters.[15,16] Xe-129 NMR was used in 1990 by Wernet et. al. to determine average micropore diameters in Illinois #6 bituminous coal.[15] After performing Xe-129 NMR experiments on spherocarb, which gave results very close to the manufacturer's specifications of microporosity, they found that the average micropore diameter of Illinois #6 coal was 5.2 Å.[15] More recently, in 1991, Tsiao and Botto use this technique to determine the average micropore size of APCS coals and to investigate the effect of weathering on the average micropore size of coals.[16] This information was then used to develop a model to approximate pore sizes and pore size swelling chacteristics.[16]

<u>EPR spin probe method</u>: Finally, a technique using EPR to follow the inclusion of molecular probes in the micropore structure has been used to determine pore size and shape characteristics of a range of coals during the swelling process.[17,18-23] This technique has also been used to follow changes in the micropore structure during weathering, oxidation, dehydration and short term oxidation.[24,26-30] The EPR spin probe method was first used to study coal by Silbernagel et. al. in 1981.[17] Later, in 1985, Wuu and Kispert expanded this technique to determine micropore size distributions in coal during swelling.[18] This EPR spin probe technique was further developed in this lab to study micropore size distributions and acid / base character of various ranked coals.[19-21] More recently, changes in pore structure and wall chemistry of APCS coals upon swelling at different temperatures and with solvents of various polarities were determined by following the retention characteristics of the coals.[22,23] The results showed that as the polarity of the solvent was increased, the shape of the micropores changed from spherical to cylindrical.[22,23] Additional studies employing EPR spin probe techniques were performed on the breaking up of the hydrogen bonding between bedding planes.[24] To gain insight into the accessible nature of the covalently cross-linked materials during swelling, the EPR spin probe method was used during the swelling of polystyrene-divinylbenzene copolymers which were cross-linked covalently to various extents (2% to 12%).[25] The study showed that hydrogen bonding in coal has a much greater impact than % cross-linking on the micropore structure and swelling character of coal. Despite this, significant amounts of guest molecules could be intercalated into the copolymer structure, even though the copolymers were relatively non-porous.[25] The effect of weathering on the structure and molecular accessibility of spin probes in coal was studied using the EPR spin probe technique.[26] It was shown that after seven days of exposure to air, coals of most ranks exhibited significant changes in spin probe retention.[26] The lower ranked coals (Beulah Zap and Wyodak Anderson), were observed to undergo structural collapse which precluded retention of even the smallest probes, while medium ranked coals actually exhibited improved retention.[26] A detailed analysis of the data collected from the swelling of coals oxidized in a moisture free environment was completed to differentiate between oxidation and the weathering process.[27,28] Eight vacuum dried APCS coals were oxidized in a pure O_2 environment and weathered in air, and the effects of oxidation alone on coal structure were determine by the intercalation of EPR spin probes.[27,28] It was shown that the removal of water was primarily responsible for the structural collapse observed in low ranked coals and for the increase in retention of polar spin probes in medium ranked coals.[27] Coals oxidized in a pure oxygen environment showed an increase in retention by as much as a factor of five.[28] Even the higher ranked coals showed significant retention of polar spin probes after four days of exposure to oxygen.[28] Studies of short term exposure of Illinois #6 to dry Argon and Oxygen were accomplished using the EPR spin probe technique.[29] It was determined that exposure to a dry gas could affect dramatic changes in the coal structure in as little as 30 seconds.[29] Currently, more detailed analyses of the effects of long term weathering for as long as six months have been carried out and will be discussed further in this paper.

EXPERIMENTAL

Samples of eight APCS coals (Beulah Zap, Wyodak Anderson, Blind Canyon, Illinois #6, Lewis Stockton, Pittsburgh #8, Upper Freeport and Poccahontas #3, defined previously[30]) were stored in vials which were exposed to the air but protected from dust or other contaminants during the period of exposure. During the weathering period, the samples were agitated each day to insure complete exposure of the coal to the air. At various points during the weathering period of six months, samples were swelled in one millimolar solutions of each spin probe in the swelling solvents toluene and pyridine. The spin probes used for this study are shown in Figure 1, VI (3-carboxy-2,2,5,5-tetramethylpyrrolidine-1-oxyl), VII (TEMPAMINE) and VIII (TEMPO). 30 mg of each coal was mixed with 2mLs of the pyridine or toluene spin probe solution. The mixture was then stirred for 18 hours so that the swelling would reach an equilibrium. The coal was then filtered and vacuum dried for 2 hours. After this the samples were washed with cyclohexane, a non-swelling solvent, to remove any spin probes on the surface or any spin probes not trapped in the coal structure. The samples were again vacuum dried and then sealed in the evacuated EPR tubes. The concentration of spins in each sample was calculated from the EPR spectra as previously described.[19]

RESULTS AND DISCUSSION

The concentration of spin probe VII retained in weathered APCS coals after swelling is shown as a function of rank and days of oxidation in Figure 2. The front edge at zero days of oxidation represents the retention of spin probe VII in fresh coals as a function of rank. Since toluene does not swell coal to a large extent, the data represents changes in structure and active site functionality during the weathering process which facilitate or inhibit interaction and retention of the polar amino spin probe. It can be seen at b_0 that the retention of fresh Beulah Zap (74.05% carbon dmmf) is about 2800×10^{15} spins per gram. This concentration drops to about 1000×10^{15} spins per gram after 7 days of weathering. By comparing these data with the retention of spin probe VIII, it has been previously determined that this decrease is caused by a physical collapse of the structure brought about by water removal.[26] After 14 days of weathering, shown at b_{14}, Beulah Zap does not show much change. However, extending the weathering period out to 36 days and even further to 64 days shows a continuing drop in spin probe retention indicated at b_{36} and b_{64}. There is a slight increase as the period of exposure to air reaches 114 days, shown at b_{114}, but essentially the following changes are relatively small compared to the weathering period. It has been shown previously during exposure to pure oxygen in a dry environment, that oxidative changes in Beulah Zap will reopen the structure to polar spin probes. This clearly is not the case during exposure to air, and it can be inferred from this data that the presence of moisture in the air inhibits oxidation in Beulah Zap lignite.

The retention character of Illinois #6 (80.73% carbon dmmf) can be similarly tracked on the three dimensional plot shown in Figure 2. The retention of spin probe VII in fresh Illinois #6 is about 750×10^{15} spins per gram as shown at i_0. An increase in retention is observed after 7 days of exposure shown at i_7 to about 2800×10^{15} spins per gram. This is followed at 14 days of exposure by a decrease in retention to about 1200×10^{15} spins per gram indicated at i_{14}. At 36 days of exposure, the retention of the spin probe is increased to 2300×10^{15} spins per gram as shown by i_{36}. It seems that an equilibrium is reached at 36 days, for further weathering has little effect on spin probe retention shown at i_{64}, i_{114} and i_{180}. The initial increase in spin probe retention in Illinois #6 is attributed to removal of water from active sites with minimal collapse of the physical structure. Since the water loss in Illinois #6 has not reached an equilibrium by 14 days,[27] it can be asserted that a partial collapse inhibits the retention of spin probes at this point. The changes which bring about the increase in retention at 36 days must be primarily due to oxidative changes in the coal structure since the water loss has reached an equilibrium by this point.

It can be seen in Figure 2 that higher ranked coals are also affected by the weathering process. Fresh Upper Freeport coal (88.08% carbon dmmf) exhibits almost no retention of spin probe VII, as shown at u_0. As the coal is weathered for 7 days, an increase in retention is observed, shown at u_7. This increase reaches over an order of magnitude as the weathering period is extended to 14 days at u_{14}. This represents the maximum retention of Upper Freeport coal, for a decrease in retention is observed at 36 days and no further changes are observed after this. Like Illinois #6, the accessibility of Upper Freeport coal seems to reach an equilibrium at 36 days of exposure to air.

A two dimensional plot of the retention of spin probe VII is shown in Figure 3 for Beulah Zap, Illinois #6 and Upper Freeport coals. It can be more easily seen in this plot that little change is affected after a weathering period of 36 days. However the same is not true for Wyodak

Anderson (76.04% carbon dmmf), Blind Canyon (81.32% carbon dmmf) and Lewis Stockton (85.47% carbon dmmf) coals (shown in Figure 4), which undergo changes throughout the 6 month weathering period studied. This would indicate that oxidation does continue throughout this period. Some comparison to data collected for long term weathering of coals swelled in pyridine might provide additional insight into this process.

CONCLUSION

It has been shown through the study of the collapse of the Beulah Zap structure, that the presence of moisture in air can inhibit oxidational changes. The structure of Illinois #6 is made much more accessible by long term weathering, and very little change of the structure is observed by monitoring the amino spin probe. Even the higher ranked coals are made more accessible during the weathering process, although this accessibility reaches a maximum after 14 days for Upper Freeport coal. Many of the coals do not exhibit continuing changes in retention of spin probe VII after 36 days.

ACKNOWLEDGMENT

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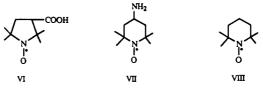
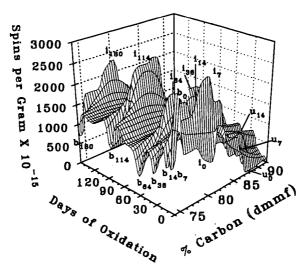Figure 1. Spin probes VI, VII, and VIII.

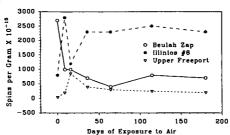Fig.2 Spin probe VII concentration in fresh APCS coals weathered in air and swelled in toluene.

Fig.3 Spin probe VII concentration in fresh APCS Beulah Zap, Illinios #6 and Upper Freeport coals weathered in air and swelled in toluene
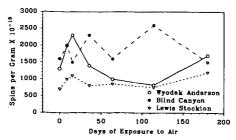

Fig.4 Spin probe VII concentration in fresh APCS Wyodak Anderson, Blind Canyon and Lewis Stockton coals weathered in air and swelled in toluene